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TITLE: Catalyst for exhaust gas purification - consists of sub-layer, intermediate layer and surface layer having specific composition laminated sequentially

PATENT-ASSIGNEE: NISSAN MOTOR CO LTD[NSMO]

PRIORITY-DATA: 1997JP-0323985 (November 11, 1997)

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INT-CL (IPC): B01D053/86, B01D053/94, B01J029/064, F01N003/28

ABSTRACTED-PUB-NO: JP 11138006A

BASIC-ABSTRACT:

NOVELTY - The catalyst has honeycomb structure of sub-layer, intermediate layer and surface layer laminated sequentially. The sub-layer contains alkali, alkaline or rare earth elements, selected from Pt, Pd or Rh. The intermediate layer has beta zeolite, while the surface layer has zeolite containing copper and/or cobalt. DETAILED DESCRIPTION - An INDEPENDENT CLAIM is also included for the exhaust gas purification method.

USE - For purifying exhaust gas ejected from internal combustion engine of motor vehicle and also from combustor.

ADVANTAGE - The purification of the lean exhaust gas in a low temperature region and low HC/NO_x ratio is raised sharply. Environment pollution due to motor vehicle exhaust is minimized by effective exhaust gas purification.

CHOSEN-DRAWING: Dwg. 1/2

TITLE-TERMS: CATALYST EXHAUST GAS PURIFICATION CONSIST SUB LAYER INTERMEDIATE LAYER SURFACE LAYER SPECIFIC COMPOSITION LAMINATE SEQUENCE

DERWENT-CLASS: E36 H06 J04 Q51

CPI-CODES: E10-J02D; E11-Q02; E31-H01; H06-C03; J01-E02D; J04-E04; N01-A; N01-B; N02-E02; N02-F; N03-A; N06-B; N06-E;

CHEMICAL-CODES:

Chemical Indexing M3 *01*

A
Wrong
Sequence
of
layers

Fragmentation Code
A100 A200 A313 A545 A546 A678 A700 A940 B114 C108
C810 M411 M730 M903 Q421

Chemical Indexing M3 *02*
Fragmentation Code
M210 M211 M212 M213 M214 M215 M216 M220 M221 M222
M223 M224 M225 M226 M231 M232 M233 M320 M416 M610
M620 M750 M903 M904 N164 Q431 Q436 Q439
Specific Compounds
90120K 90120X

Chemical Indexing M3 *03*
Fragmentation Code
C106 C108 C550 C730 C800 C801 C802 C803 C805 C807
M411 M750 M903 M904 M910 N164 Q431 Q436 Q439
Specific Compounds
01423K 01423X
Registry Numbers
1423U

Chemical Indexing M3 *04*
Fragmentation Code
C107 C108 C307 C520 C730 C800 C801 C802 C803 C804
C807 M411 M750 M903 M904 M910 N164 Q431 Q436 Q439
Specific Compounds
01784K 01784X
Registry Numbers
1784U

UNLINKED-DERWENT-REGISTRY-NUMBERS: 1423U; 1784U

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(54)【発明の名称】 排気ガス浄化用触媒及び浄化方法

(57)【要約】

【課題】 低温域及び低HC/NOx比におけるリーン排ガス中のNOx浄化能を大幅に向上させ、且つ高温水熱条件下においても触媒の劣化を防止した排気ガス浄化用触媒及び浄化方法を提供すること。

【解決手段】 ハニカム状モノリス担体上に、下層、中間層及び表層を順次積層して成る触媒である。下層が、白金、パラジウム及びロジウムから成る群より選ばれた少なくとも1種の成分と、アルカリ金属、アルカリ土類金属及び希土類元素から成る群より選ばれた少なくとも1種の成分とを含有し、中間層が、 β -ゼオライトを含有し、表層が、銅及び/又はコバルトを含むゼオライトを含有する。

等から排出される排気ガスを浄化するための触媒に係り、理論空燃比より高い空燃比で運転されるエンジンの排気ガス（以下「リーン排ガス」という。）の窒素酸化物（以下「NO_x」という。）を高効率で浄化するための触媒及び浄化方法に関するものである。

【0002】

【従来の技術】従来、自動車エンジンから排出されるガスのように酸化成分と還元成分をほぼ等しく含む排気ガスを浄化するための触媒には、三元触媒が幅広く用いられている。この触媒は、白金、パラジウム、ロジウム等の貴金属及びセリアをはじめとする各種成分を担持した活性アルミナを主成分とする触媒であり、排気ガス中の有害成分である炭化水素（以下「HC」という。）、一酸化炭素（以下「CO」という。）及びNO_xを高効率で浄化することができる。

【0003】一方、近年、燃費の向上や二酸化炭素の排出量の削減という観点から、理論空燃比より高い空燃比でも運転するリーンバーンエンジンが注目されている。このようなエンジンからのリーン排ガスは、理論空燃比の近傍で運転するエンジンからの排ガス（ストイキ排ガス）に比べて酸素含有率が高いため、上記三元触媒では、NO_xの反応相手となるべきCOやHCの還元性ガスがほとんど酸素に食われてしまい、NO_xの浄化が不十分となることから、リーン排ガスのNO_xを高効率で浄化することができる新触媒が望まれていた。

【0004】このような状況において、銅、コバルト、銀、ニッケル、鉄等の遷移金属や白金等の貴金属をY型、L型、モルデナイト、MFIゼオライト等のゼオライトに担持したゼオライト系触媒は、HCの共存下でリーン排ガス中のNO_xを比較的効率よく浄化することができる能力を有している。特に銅をゼオライトに担持した銅-ゼオライト系触媒は、高流速ガス条件下であっても比較的優れたNO_x浄化能を示すことから、自動車のような小型移動発生源や安定型の自家発電用エンジン等の排気ガスの浄化への適用に期待がかけられていた。

【0005】ところが、上記金属を担持したゼオライト系触媒には、150～300°Cの低温域で十分にNO_xを浄化することができないこと、NO_xとHCが反応してNO_xをN₂に転化するのに必要なHCとNO_xとの比率（以下「HC/NO_x比」という。）が5～6以下になると、NO_x浄化率が急激に低下すること、600°C以上の水蒸気を含む高温条件（水熱条件）下では触媒の劣化が極めて大きいこと等の問題点があるため、リーンバーンエンジンの排気ガス浄化用触媒として実用化に至っていない。

【0006】これに対し、銅-ゼオライト系触媒層の下層に貴金属層を設けることにより、貴金属層で発生する酸化反応熱を利用して、より低温から上層の銅-ゼオライト系触媒を作動させ、低温におけるNO_x浄化率を向上させることが、特開平1-127044号公報及び特

【特許請求の範囲】

【請求項1】 ハニカム状モノリス担体上に、下層、中間層及び表層を順次積層して成る排気ガス浄化用触媒であって、

上記下層が、白金、パラジウム及びロジウムから成る群より選ばれた少なくとも1種の成分と、アルカリ金属、アルカリ土類金属及び希土類元素から成る群より選ばれた少なくとも1種の成分とを含有し、

上記中間層が、βゼオライトを含有し、

上記表層が、銅及び/又はコバルトを含むゼオライトを含有することを特徴とする排気ガス浄化用触媒。

【請求項2】 上記アルカリ金属、アルカリ土類金属及び希土類元素が、マグネシウム、カルシウム、カリウム、バリウム、ランタン、ストロンチウム、セシウム及びセリウムから成る群より選ばれた少なくとも1種のものであることを特徴とする請求項1記載の排気ガス浄化用触媒。

【請求項3】 上記アルカリ金属、アルカリ土類金属及び希土類元素から成る群より選ばれた少なくとも1種の成分の含有量が、当該排気ガス浄化用触媒1L当たり0.1～0.6モルであることを特徴とする請求項1又は2記載の排気ガス浄化用触媒。

【請求項4】 上記βゼオライトのシリカ/アルミナ比が20～150であることを特徴とする請求項1～3のいずれか1つの項に記載の排気ガス浄化用触媒。

【請求項5】 上記中間層の担持量が当該排気ガス浄化用触媒1L当たり20～100gであることを特徴とする請求項1～4のいずれか1つの項に記載の排気ガス浄化用触媒。

【請求項6】 上記表層が含有するゼオライトのシリカ/アルミナ比が20～80であることを特徴とする請求項1～5のいずれか1つの項に記載の排気ガス浄化用触媒。

【請求項7】 上記表層の担持量が当該排気ガス浄化用触媒1L当たり120～300gであることを特徴とする請求項1～6のいずれか1つの項に記載の排気ガス浄化用触媒。

【請求項8】 請求項1～7のいずれか1つの項に記載の排気ガス浄化用触媒を用いた排気ガス浄化方法であつて、

空燃比が1.4.7以上で運転される内燃機関の排気系に、上記排気ガス浄化用触媒を設置し、

この排気ガス浄化用触媒に、酸素濃度が5%以上で、且つ窒素酸化物と炭化水素が反応して窒素酸化物を窒素に転化するのに必要な炭化水素量と窒素酸化物量との比率であるHC/NO_x比が10以下の排気ガスを流通、接触させることを特徴とする排気ガス浄化方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、内燃機関、燃焼器

開平5-68888号公報に開示されている。また、白金系触媒を用いれば、200~250°Cの比較的低温域であっても、NO_xをN₂に転化することが可能であることも知られている。一方、低HC/NO_x比の排気ガスでは、銅-ゼオライト系触媒、白金系触媒のいずれの場合にもNO_x浄化能が不十分となることから、還元剤として作用するHC、アルコール類等を触媒の入口に二次的に供給する方法が提案されている。

【0007】

【発明が解決しようとする課題】しかし、銅-ゼオライト触媒層の下層に貴金属層を設けた場合、貴金属層における反応熱のために劣化が大きくなるだけでなく、貴金属層の強い酸化活性のためにHCが優先的に酸化消費されることから、NO_xの浄化率を十分に向上することができないという課題があった。これは、特開平1-31074号公報及び特開平5-168939号公報に記載された銅-ゼオライト系触媒層に貴金属を共存させた場合には特に大きくなる。

【0008】また、白金系触媒を使用した場合には、NO_xからN₂への転化の際に生成されるN₂Oを無視することができず、環境への悪影響を回避するためにも、そのまま使用することはできないという課題があった。さらに、還元剤を二次的に補給するためには、還元剤用のタンクを車載するか又は燃料に還元剤を混入する必要があるが、タンクを車載する場合には、その収納場所の確保が困難であることやタンクの搭載により重量が増加する等の問題があった。還元剤を直接混合する場合には、燃費が低下するという問題があった。従って、排気温度及びHC/NO_x比が低いリーンバーンエンジンの排気ガスに有効な浄化用触媒及び浄化方法はないのが実状である。

【0009】本発明は、このような従来技術の有する課題に鑑みてなされたものであり、その目的とするところは、低温域及び低HC/NO_x比におけるリーン排気ガス中のNO_x浄化能を大幅に向上させ、且つ高温水熱条件下においても触媒の劣化を防止した排気ガス浄化用触媒及び浄化方法を提供することにある。

【0010】

【課題を解決するための手段】本発明者らは、上記課題を解決すべく鋭意検討した結果、ハニカム担体上に特定の機能を有する三つの触媒層を配置することにより、低温域及び低HC/NO_x比におけるリーン排気ガス中のNO_x浄化能を大幅に向上させ、且つ高温水熱条件下においても触媒の劣化を防止することができるを見出し、本発明を完成するに至った。

【0011】即ち、本発明の排気ガス浄化用触媒は、ハニカム状モノリス担体上に、下層、中間層及び表層を順次積層して成る排気ガス浄化触媒であって、上記下層が、白金、パラジウム及びロジウムから成る群より選ばれた少なくとも1種の成分と、アルカリ金属、アルカリ

土類金属及び希土類元素から成る群より選ばれた少なくとも1種の成分とを含有し、上記中間層が、βゼオライトを含有し、上記表層が、銅及び/又はコバルトを含むゼオライトを成分として含有することを特徴とする。

【0012】また、本発明の排気ガス浄化方法は、空燃比が14.7以上のリーン条件で運転される内燃機関の排気系に、上記排気ガス浄化用触媒を設置し、この排気ガス浄化用触媒に酸素濃度が5%以上で、且つHC/NO_x比が10以下の排気ガスを流通、接触させることを特徴とする。

【0013】

【作用】本発明の排気ガス浄化用触媒では、ハニカム状担体に、下層、中間層及び表層を順次積層したが、これらの層は、それぞれNO_x吸着材、HC吸着材及びNO_x還元材として機能する。

【0014】即ち、下層はNO_xを酸化してより反応性の高いNO_xに転換し、表層のNO_x還元材の低温活性を促進する。また、中間層は、排ガス低温時にHC類を効率よくトラップし、表層のNO_x還元材が作動する温度域になるとトラップしたHC類を放出し、表層によるNO_x還元を促進する。更に、下層及び中間層は、高水熱条件下で劣化した表層のNO_x酸化能及びHC吸着とその改質作用を補うので、触媒全体として高温水熱条件下での触媒劣化が抑制される。

【0015】なお、上述した積層構造において、表層は最表面に、下層は最下層に配置することが好ましいが、かかるNO_x還元材層と貴金属触媒層とを直接接觸させると、活性成分同士の反応が起こるなど、触媒劣化の面で好ましくないことがある。よって、本発明の触媒では、中間層にβゼオライトを配置してかかる不具合を回避するとともに、HC吸着をも実現している。

【0016】

【発明の実施の形態】以下、本発明の排気ガス浄化用触媒について詳細に説明する。上述の如く、本発明の排気ガス浄化用触媒は、リーンバーンエンジンに好適な排気ガス浄化用触媒であって、ハニカム状担体上に、貴金属やアルカリ金属等を担持したNO_x吸着層（下層）、βゼオライトを含有するHC吸着層（中間層）、及び銅-ゼオライト系触媒等を含むNO_x還元層（表層）を順次積層して成る。

【0017】ここで、下層に含まれるアルカリ金属、アルカリ土類金属及び希土類元素としては、マグネシウム、カルシウム、カリウム、バリウム、ランタン、ストロンチウム、セシウム又はセリウム及びこれらの任意の組み合わせを挙げることができ、その含有量は、得られる排気ガス浄化用触媒1L当たり0.1~0.6モルとすることが好ましい。含有量が1L当たり0.1モル未満では、含有させた貴金属の効果が十分には發揮されず、逆に0.6モルを超えると、貴金属の効果が打ち消されることがあり、好ましくない。

【0018】また、中間層に含有される β ゼオライトのシリカ／アルミナのモル比（以下「シリカ／アルミナ比」という。）は、20～150であることが好ましい。シリカ／アルミナ比が20未満の場合には、ゼオライト骨格が不安定になり、逆に150を超えると、HCを保持する力が弱くなつて表層が作動を開始する温度までHCを蓄えることができなくなることがあります、好ましくない。なお、 β ゼオライトを含有する中間層の担持量は、得られる排気ガス浄化用触媒1L当たり20～100gとすればよい。

【0019】表層に含有されるゼオライトとしては、Y型ゼオライト、フェリエライト、モルデナイト等を挙げることができるが、特にシリカ／アルミナ比が20～80のMFIゼオライト及び／又は β ゼオライトを好ましく使用することができます。シリカ／アルミナ比が20の未満では、ゼオライト骨格が不安定になると同時にイオン交換で担持される活性成分（銅及び／又はコバルト）の量が過剰となり、分散性が低下して活性点1点当たりの活性が急激に低下するととともに、活性点同士の凝集が起りやすくなつて、いわゆるシンタリングによる劣化が進行し易くなり、逆に80を超えると、活性点の数が少なすぎて十分な活性が得られないことがあります、好ましくない。

【0020】また、上述した表層の担持量は、得られる排気ガス浄化用触媒1L当たり120～300gとすることが好ましい。担持量が1L当たり120g未満では、高SV下での活性が不十分となり、逆に300gを超えると、下層及び中間層への反応分子の拡散を妨げたり、圧力損失が大きくなるなどの悪影響が生じることがあり、好ましくない。

【0021】なお、上述した中間層及び表層に用いるゼオライトは、そのままで無処理のものであつてもよいが、水熱処理や再合成を行うことによって結晶性を高めるとより安定化し、耐熱性及び耐久性の高い触媒が得られるので、本発明では、このような処理を施したゼオライトを使用することが好ましい。

【0022】また、本発明の触媒では、ハニカム形状のモノリス担体を使用して、下層、中間層及び表層の多層化を実現するが、この場合、ハニカム状の担体に上述したゼオライト系触媒や貴金属成分等を塗布して多層化を行えばよい。このハニカム材料としては、一般にコーチェライト質のものが広く用いられているが、これに限定されるものではなく、金属材料から成るハニカム担体を用いることもできる。

【0023】なお、触媒の形状をハニカム状とすれば、触媒と排ガスとの接触面積を大きくでき、圧力損失を抑えることができるため、振動があり、且つ限られた空間内で多量の排ガスを処理することが要求される自動車用触媒として用いる場合には、特に有利である。

【0024】次に、本発明の触媒の製造方法について説 50

明する。本発明のハニカム状モノリス触媒は、触媒粉を水と混合してスラリーを得、このスラリーをハニカム担体にコーティングすることにより製造できる。この触媒製造において、ゼオライトに担持する金属成分の原料としては、各種金属の無機酸塩、酸化物、有機酸塩、塩化物、炭酸塩、ナトリウム塩、アンモニウム塩及びアンミン錯化合物等の各種化合物を使用することができ、イオン交換法や含浸法等の通常用いられる方法で担持することができる。

10 【0025】なお、通常のイオン交換法、含浸法による場合、金属原料は溶液で用いることが多い、その溶液に酸又は塩基を添加して適当にpHを調節することにより、好ましい結果を得られることもあるが、本発明はこのような担持法によって制限されるものではない。

【0026】以上に説明してきた本発明の排気ガス浄化用触媒は、空燃比が14.7以上のリーン条件で運転される内燃機関からの排気ガスに対して浄化作用を示すものであるが、特に酸素濃度が5%以上で、且つHC/N_Ox比が1.0以下の排気ガスを本触媒に流通、接触させると、高効率な排気ガス浄化が実現される。また、本触媒は、このような排気ガス条件下では長時間の使用にも十分に耐え、高い浄化性能を維持するが、酸素濃度が低く、HCの量が多すぎると、触媒表面上へのコーティングが起り易くなり、触媒の劣化が促進されることがある。

【0027】

【実施例】以下、本発明を実施例及び比較例により更に詳細に説明するが、本発明はこれら実施例に限定されるものではない。

30 【0028】（実施例1）

（1）下層の形成

ジニトロジアンミン白金水溶液中に活性アルミナの粉末を添加してよく攪拌し、120℃で8時間乾燥した後、空気流中500℃で2時間焼成し、白金を約1.0wt%担持したPt－活性アルミナ粉末を得た。この粉末と硝酸酸性アルミナゾルと水とを磁性ポールミルポットに入れ、約20分間混合・粉碎してPt－活性アルミナのスラリーを得た。なお、この際のアルミナゾルの添加量は5wt%とした。

40 【0029】このようにして得られたスラリーを1平方インチ断面当たり約400個の流路を持つコーチェライト質ハニカム担体1.0Lに塗布し、150℃で熱風乾燥した後、500℃で1時間焼成してコート量約35g/Lのハニカム触媒を得た。このハニカム触媒を酢酸カルシウム、酢酸バリウム及び硝酸ランタンを含む混合水溶液に浸し、120℃で乾燥した後、500℃で1時間焼成して、カルシウム、バリウム及びランタンをハニカム触媒1リットル当たりそれぞれ0.1モル、0.15モル及び0.1モルを担持したハニカム触媒A₁を得た。

- 【0030】(2) 中間層の形成
シリカ/アルミナ比が約3.5のH型 β ゼオライトの粉末にアルミナゾルと水を加え、磁性ポールミルポットに入れて約20分間混合・粉碎し、 β ゼオライトのスラリーを得た。なお、この際のアルミナゾルの添加量はA₁₂O₃として8wt%とした。次いで、得られたスラリーを上記ハニカム触媒A₁に塗布し、150°Cで熱風乾燥した後、500°Cで1時間焼成して、ハニカム触媒A₁の下層上に約5.5g/Lの中間層を積層したハニカム触媒A₂を得た。
- 【0031】(3) 表層の形成、3層積層触媒の完成
濃度0.17Mの硝酸銅及び硝酸コバルト混合水溶液(銅:コバルト=8:2)中にシリカ/アルミナ比が約3.5のNH₄型MFⅠゼオライトの粉末を添加してよく攪拌した後、沪過して固液を分離した。かかる攪拌・沪過操作を3回繰り返して、銅及びコバルトをイオン交換担持したMFⅠゼオライト触媒ケーキを得た。
- 【0032】得られたケーキを120°Cで24時間以上乾燥し、次いで、大気雰囲気下600°Cで4時間焼成して、銅が3.9wt%、コバルトが0.8wt%を担持されたCu-Co-MFⅠ触媒粉末を得た。この触媒粉末をアルミナゾル及び水と混合し、磁性ポールミルポットで20分間粉碎してスラリーとした。このようにして得られたスラリーを上記ハニカム状触媒A₂にコーティングし、120°Cで8時間乾燥した後、空気流中450°Cで1時間焼成して、触媒A₂の中間層上に約200g/Lの表層を積層した実施例1の3層構造触媒を得た。
- 【0033】(実施例2) 表層のMFⅠゼオライト粉末をシリカ/アルミナ比が約4.2のNH₄型 β ゼオライトに代えた以外は、実施例1と同様の操作を繰り返し、本例の触媒を得た。
- 【0034】(実施例3) 下層における貴金属担持量であるPt担持1.0wt%を、Pd担持1.2wt%及びRh担持0.2wt%に代えた以外は実施例1と同様の操作を繰り返し、本例の触媒を得た。
- 【0035】(実施例4) 下層におけるアルカリ金属等の含有量であるカルシウム0.1モル、バリウム0.15モル及びランタン0.1モルを、マグネシウム0.01モル、バリウム0.01モル及びカリウム0.01モルに代えた以外は、実施例1と同様の操作を繰り返し、本例の触媒を得た。
- 【0036】(実施例5) 下層におけるアルカリ金属等の含有量であるカルシウム0.1モル、バリウム0.15モル及びランタン0.1モルを、バリウム0.2モル、ストロンチウム0.05モル、セシウム0.04モル及びセリウム0.29モルに代えた以外は、実施例1と同様の操作を繰り返し、本例の触媒を得た。
- 【0037】(実施例6) 表層コート量200g/Lを130g/Lに代えた以外は、実施例1と同様の操作を繰り返し、本例の触媒を得た。
- 【0038】(実施例7) 表層コート量200g/Lを280g/Lに代えた以外は、実施例1と同様の操作を繰り返し、本例の触媒を得た。
- 【0039】(実施例8) 中間層コート量5.5g/Lを2.5g/Lに代えた以外は、実施例1と同様の操作を繰り返し、本例の触媒を得た。
- 【0040】(実施例9) 中間層コート量5.5g/Lを9.6g/Lに代えた以外は、実施例1と同様の操作を繰り返し、本例の触媒を得た。
- 【0041】(実施例10) 表層のMFⅠゼオライトをシリカ/アルミナ比が約2.4のH型MFⅠゼオライトに代えた以外は、実施例1と同様の操作を繰り返し、本例の触媒を得た。
- 【0042】(実施例11) 表層のMFⅠゼオライトをシリカ/アルミナ比が約7.6のH型MFⅠゼオライトに代えた以外は実施例1と同様の操作を繰り返し、本例の触媒を得た。
- 【0043】(比較例1) 中間層を設けずに下層上に表層を積層した以外は、実施例1と同様の操作を繰り返し、本例の触媒を得た。
- 【0044】(比較例2) 中間層の β ゼオライトを γ アルミナに代えた以外は、実施例1と同様の操作を繰り返し、本例の触媒を得た。
- 【0045】(実施例12) 下層におけるマグネシウム0.01モル、バリウム0.1モル及びカリウム0.01モルをマグネシウム0.03モル、バリウム0.04モル及びカリウム0.01モルに代えた以外は、実施例4と同様の操作を繰り返し、本例の触媒を得た。
- 【0046】(実施例13) 下層におけるバリウム0.2モル、ストロンチウム0.05モル、セシウム0.04モル及びセリウム0.29モルを、バリウム0.3モル、ストロンチウム0.02モル、セシウム0.3モル及びセリウム0.01モルに代えた以外は、実施例5と同様の操作を繰り返し、本例の触媒を得た。
- 【0047】(実施例14) 表層コート量130g/Lを100g/Lに代えた以外は、実施例6と同様の操作を繰り返し、本例の触媒を得た。
- 【0048】(実施例15) 表層コート量130g/Lを320g/Lに代えた以外は、実施例6と同様の操作を繰り返し、本例の触媒を得た。
- 【0049】(実施例16) 中間層コート量2.5g/Lを1.7g/Lに代えた以外は、実施例8と同様の操作を繰り返し、本例の触媒を得た。
- 【0050】(実施例17) 中間層コート量2.5g/Lを1.15g/Lに代えた以外は、実施例8と同様の操作を繰り返し、本例の触媒を得た。
- 【0051】(実施例18) 表層のMFⅠゼオライトをシリカ/アルミナ比が約1.7のH型MFⅠゼオライトに代えた以外は、実施例10と同様の操作を繰り返し、本例の触媒を得た。

【0052】(実施例19)表層のMFIゼオライトをシリカ／アルミナ比が約8.2のH型MFIゼオライトにえた以外は、実施例10と同様の操作を繰り返し、本例の触媒を得た。

【0053】(触媒性能試験例1)上記各例の触媒をリーンバーンエンジンの一例である4気筒2.5Lディーゼルエンジンを設置したエンジンダイナモ装置の排気系に組み込み、630°Cで30時間の急速耐久処理を行った。次いで、このように処理した各例の触媒を上記同様のエンジンダイナモ装置の排気系に組み込み、触媒入口温度100°C～500°Cの昇温時におけるNOx転化性能*

*を測定した。この際、100～500°Cの昇温速度は約30°C/min、排気ガス中の平均HC/NOx比は2.8、ガス空間速度は45000h⁻¹であった。なお、このエンジンダイナモ装置では、エンジンマニホールドと触媒との間に設けたノズルから軽油を注入することができ、これにより、排ガス中のHC/NOxを変化させることが可能である。各例の触媒についての100～500°C昇温中の平均NOx浄化性能を表1に示す。

【0054】

10 【表1】

触媒	平均NOx浄化率(%)
実施例1	26.4
実施例2	27.5
実施例3	25.5
実施例4	21.6
実施例5	19.4
実施例6	18.9
実施例7	26.1
実施例8	21.4
実施例9	18.8
実施例10	17.7
実施例11	24.4
実施例12	17.0
実施例13	17.3
実施例14	16.9
実施例15	17.5
実施例16	17.3
実施例17	18.5
実施例18	16.4
実施例19	18.1
比較例1	12.4
比較例2	13.3

【0055】表1から、本発明の範囲に属する実施例の触媒は、比較例の触媒に比しNOx浄化率が高いが、これは、実施例の触媒が低温域でHC類を効率良くトラップし、且つこのHC類を昇温過程で高効率で利用していることを示していると考えられる。また、アルカリ金属※50

※等の担持量が好適範囲を逸脱すると、下層や表層の効果が低減することがあり、特に表層のゼオライトのシリカ／アルミナ比は触媒性能に与える影響が大きいことも分かる。更に、中間層及び表層のコート量も触媒性能に与える影響が大きいことも明かである。

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【0056】(触媒性能試験例2)実施例2の触媒を用い、上述した試験例1と同様の浄化性能試験を行った。但し、本性能試験では、排ガス中のHC濃度を変化させることによりHC/NO_x比を2~15の範囲で変化させてライトオフーライトオンを10回繰り返し、その後のHC/NO_x比に対するNO_x平均浄化率を求めた。得られた結果を図1に示す。

【0057】図1から、本発明の排気ガス浄化用触媒では、HC/NO_x比が10以下においては十分に高い浄化率が得られる一方、HC/NO_x比が10より大きくなると、NO_x浄化率が急激に低下することが分かった。この結果から、本発明の触媒は、むしろ適度なHC量で高いNO_x浄化率を実現することが分かる。

【0058】(触媒性能試験例3)実施例2の触媒を用い、上記試験例1と同様の浄化性能試験を行った。但し、本性能試験では、排気ガスの酸素濃度を2%~10%の範囲で変化させてライトオフーライトオンを10回繰り返して行い、その後、ライトオフーライトオンテストを行い、NO_xの平均浄化率を求めた。得られた結果を図2に示す。

【0059】図2から、本発明の排気ガス浄化用触媒は、排気ガスの酸素濃度が5%以上の比較的酸素量の多い条件下でライトオフーライトオンテストを繰り返す

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と、高いNO_x浄化率を発揮するが、酸素濃度が5%より少ない条件下でライトオフーライトオンテストを繰り返すと、十分なNO_x浄化性能を示さないことがあることが分かった。

【0060】

【発明の効果】以上説明してきたように、本発明によれば、ハニカム担体上に特定の機能を有する三つの触媒層を配置することとしたため、低温域及び低HC/NO_x比におけるリーン排気ガス中のNO_x浄化能を大幅に向上させ、且つ高温水熱条件下においても触媒の劣化を防止した排気ガス浄化用触媒及び浄化方法を提供することができる。

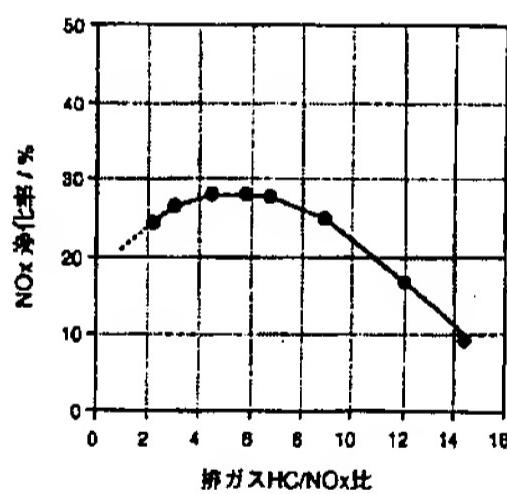
【0061】即ち、本発明の排気ガス浄化用触媒を用いると、150°C以下の低温域で且つ低HC/NO_x比においても、リーン排ガスを高効率で浄化することができるため、本触媒はリーンバーンエンジンに好適であり、また、環境汚染が少なく経済性にも優れた自動車を実現することも可能になる。

【図面の簡単な説明】

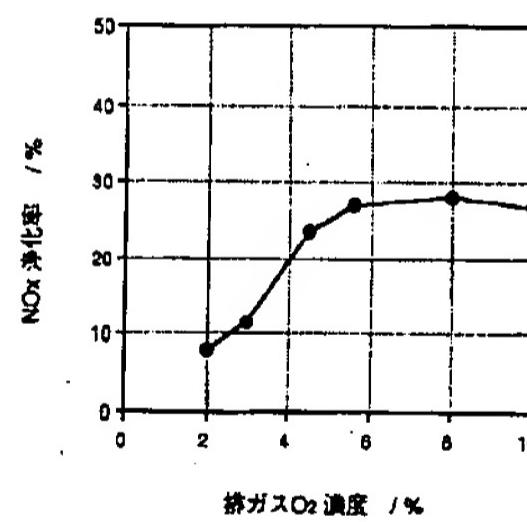
20 【図1】NO_x浄化率に対する排ガスHC/NO_x比の影響を示すグラフである。

【図2】NO_x浄化率に対する排ガスO₂濃度の影響を示すグラフである。

【図1】



【図2】



* NOTICES *

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the catalyst for purifying the exhaust gas discharged from an internal combustion engine, a combustor, etc., and relates to the catalyst and the purification method for it being efficient and purifying the exhaust gas (henceforth "RIN exhaust gas") nitrogen oxide (henceforth "NOx") of the engine operated with an air-fuel ratio higher than theoretical air fuel ratio.

[0002]

[Description of the Prior Art] The three way component catalyst is broadly used for the catalyst for purifying conventionally the exhaust gas which contains an oxidization component and a reduction component almost equally like the gas discharged from an automobile engine. This catalyst is a catalyst which makes a principal component the activated alumina which supported various components including noble metals, such as platinum, palladium, and a rhodium, and Seria, is efficient and can purify the hydrocarbon (henceforth "HC") which is an injurious ingredient in exhaust gas, a carbon monoxide (henceforth "CO"), and NOx.

[0003] On the other hand, the lean burn engine operated also with an air-fuel ratio higher than theoretical air fuel ratio from a viewpoint of improvement in mpg or curtailment of the discharge of a carbon dioxide attracts attention in recent years. A new catalyst which the reducing gas of CO or HC which should serve as a reactional phase hand of NOx in the above-mentioned three way component catalyst will almost be consumed by oxygen, and is [be / inadequate / purification of NOx] efficient in NOx of a bird clapper to RIN exhaust gas since oxygen content is high, and can be purified compared with the exhaust gas (SUTOIKI exhaust gas) from the engine which operates the RIN exhaust gas from such an engine near the theoretical air fuel ratio was desired.

[0004] In such a situation, the zeolitic catalyst which supported noble metals, such as transition metals, such as copper, cobalt, silver, nickel, and iron, and platinum, to zeolites, such as Y type, an L type, a mordenite, and a MFI zeolite, has the capacity which can purify NOx in RIN exhaust gas comparatively efficiently under coexistence of HC. Since the comparatively excellent NOx decontamination capacity was shown even if the copper-zeolitic catalyst which supported especially copper to the zeolite was under the high rate-of-flow gas condition, expectation was applied to application to purification of exhaust gas, such as small mobile emission sources like an automobile, and a stable type engine for private power generation.

[0005] however, to the zeolitic catalyst which supported the above-mentioned metal The ratio of HC and NOx required for NOx and HC to react and convert [that NOx cannot fully be purified in a 150-300-degree C low-temperature region, and] NOx into N2 (it is called a "HC/NOx ratio" below.) If it becomes five to six or less, since there are troubles, like that the rate of NOx purification falls rapidly and degradation of a catalyst is very large under the high temperature service (hydrothermal conditions) containing a steam 600 degrees C or more, it has not resulted in utilization as a catalyst for exhaust air gas cleanups of a lean burn engine.

[0006] On the other hand, by preparing a noble-metals layer in the lower layer of a copper-zeolitic-catalyst layer, using the oxidation reaction heat generated in a noble-metals layer, the upper copper-zeolitic catalyst is operated more from low temperature, and raising the rate of NOx purification in low temperature is indicated by JP,1-127044,A and JP,5-68888,A. Moreover, if a platinum system catalyst is used, even if it is a low-temperature region comparatively, it is known that the 200-250-degree C thing for which NOx is converted into N2 is also possible. On the other hand, in the exhaust gas of a low HC/NOx ratio, the method of supplying secondarily HC which acts from a bird clapper that NOx decontamination capacity is inadequate as a reducing agent, alcohols, etc. to the entrance of a catalyst in any [of a copper-zeolitic catalyst and a platinum system catalyst] case is proposed.

[0007]

[Problem(s) to be Solved by the Invention] However, when a noble-metals layer was prepared in the lower layer of a copper-zeolite-catalyst layer, since oxidization consumption of the HC was preferentially carried out for the strong oxidization activity of a noble-metals layer, not only degradation benefits large the heat of reaction in a noble-metals layer, but the technical problem that the rate of purification of NOx could not fully be improved occurred. This becomes large especially, when noble metals are made to live together in the copper-zeolitic-catalyst layer indicated by JP,1-31074,A and JP,5-168939,A.

[0008] Moreover, when a platinum system catalyst is used, in order to be unable to disregard N₂O from NOx to N₂ generated in the case of inversion but to avoid the bad influence to environment, the technical problem that it could not be used as it is occurred. Furthermore, although the tank for reducing agents needed to be mounted or the reducing agent needed to be mixed in fuel in order to supply a reducing agent secondarily, when a tank was mounted, there was a problem of a weight increasing by loading of that reservation of the receipt place is difficult and a tank. When a reducing agent was mixed directly, there was a problem that mpg fell. Therefore, the actual condition is that there are not a catalyst for purification with an exhaust-gas temperature and a HC/NOx ratio effective in the exhaust gas of a low lean burn engine and the purification method.

[0009] this invention offers the catalyst for exhaust air gas cleanups and the purification method of the place which it is made in view of the technical problem which such conventional technology has, and is made into the purpose having raised sharply the NOx decontamination capacity in the RIN exhaust gas in a low-temperature region and a low HC/NOx ratio, and having prevented degradation of a catalyst under the high-temperature-hot-water heat condition -- i is in things

[0010]

[Means for Solving the Problem] As a result of inquiring wholeheartedly that the above-mentioned technical problem should be solved, by arranging three catalyst beds which have a specific function on honeycomb support, this inventior persons find out that the NOx decontamination capacity in the RIN exhaust gas in a low-temperature region and a low HC/NOx ratio can be raised sharply, and degradation of a catalyst can be prevented under a high-temperature-hot-wate heat condition, and came to complete this invention.

[0011] The catalyst for exhaust air gas cleanups of this invention namely, on honeycomb-like monolith support At leas one sort of components chosen from the group to which it is the exhaust air gas cleanup catalyst which carries out the laminating of a lower layer, an interlayer, and the surface one by one, and changes, and the above-mentioned lower layer changes from platinum, palladium, and a rhodium, It is characterized by containing at least one sort of components chosen from the group which consists of alkali metal, alkaline earth metal, and rare earth elements, for the above-mentioned interlayer containing beta zeolite, and the above-mentioned surface containing the zeolite containing copper and/or cobalt as a component.

[0012] Moreover, the exhaust air gas cleanup method of this invention installs the above-mentioned catalyst for exhaus air gas cleanups in the exhaust air system of the internal combustion engine with which an air-fuel ratio is operated on 14.7 or more RIN conditions, and is characterized by for an oxygen density being 5% or more, and for a HC/NOx ratio circulating and contacting ten or less exhaust gas at this catalyst for exhaust air gas cleanups.

[0013]

[Function] With the catalyst for exhaust air gas cleanups of this invention, although the laminating of a lower layer, an interlayer, and the surface was carried out to honeycomb-like support one by one, these layers function as NOx adsorption material, HC adsorption material, and NOx reduction material, respectively.

[0014] That is, a lower layer oxidizes, converts NOx into NOx with more high reactivity, and promotes the low-temperature activity of surface NOx reduction material. Moreover, an interlayer does the trap of the HC efficiently at the time of exhaust gas low temperature, emits HC which carried out the trap when it became the temperature region where surface NOx reduction material operates, and promotes the NOx reduction by the surface. Furthermore, since a lower layer and an interlayer compensate the NOx oxidization ability and HC adsorption, and its reforming operation o the surface which deteriorated under flood heat conditions, the catalyst de-activation under high-temperature-hot-water heat conditions is suppressed as the whole catalyst.

[0015] In addition, in the laminated structure mentioned above, it is not sometimes desirable, when this NOx reduction material layer and noble metal catalyst layer are contacted directly, although it is desirable to arrange a surface on the maximum front face and to arrange a lower layer in the lowest layer in respect of catalyst de-activation -- the reaction of active ingredients occurs. Therefore, with the catalyst of this invention, while arranging beta zeolite to an interlayer and avoiding this fault, HC adsorption is also realized.

[0016]

[Embodiments of the Invention] Hereafter, the catalyst for exhaust air gas cleanups of this invention is explained in

detail. Like *****, the catalyst for exhaust air gas cleanups of this invention is a suitable catalyst for exhaust air gas cleanups for a lean burn engine, on honeycomb-like support, carries out the laminating of the NOx reduction zone (surface) containing the NOx adsorption layer (lower layer) which supported noble metals and alkali-metal *****, HC adsorption layer (interlayer) containing beta zeolite, a copper-zeolitic catalyst, etc. one by one, and changes.

[0017] Here, as the alkali metal contained in a lower layer, alkaline earth metal, and rare earth elements, magnesium, calcium, a potassium, barium, a lanthanum, strontium, caesium or ceriums, and such arbitrary combination can be mentioned, and, as for the content, it is desirable to consider as 0.1-0.6 mols of catalyst 1L scaling for exhaust air gas cleanups obtained. a content – per [1L] -- if the effect of the noble metals made to contain is not fully demonstrated but exceeds 0.6 mols conversely in less than 0.1 mols, the effect of noble metals may be negated and it is not desirable

[0018] Moreover, as for the mole ratio (henceforth "a silica / alumina ratio") of the silica/alumina of beta zeolite contained in an interlayer, it is desirable that it is 20-150. If a zeolite skeleton becomes unstable and exceeds 150 conversely when a silica / alumina ratio is less than 20, the force of holding HC becomes weak, and it may be able to stop being able to store HC to the temperature to which a surface starts an operation, and is not desirable. In addition, what is necessary is just to consider the amount of support of the interlayer containing beta zeolite as per [which are obtained / catalyst 1L for exhaust air gas cleanups / 20-100g].

[0019] As a zeolite contained on a surface, although Y type zeolite, a FERIE light, a mordenite, etc. can be mentioned, a silica / alumina ratio can use preferably the MFI zeolite and/or beta zeolite of 20-80 especially. The amount of the active ingredient (copper and/or cobalt) by which a silica / alumina ratio is supported with the following of 20 according to the ion exchange while a zeolite skeleton becomes unstable becomes superfluous. As if dispersibility falls and the activity per active spot falls rapidly, both If condensation of the active spots becomes easy to take place, degradation by the so-called sintering becomes easy to advance and 80 is exceeded conversely, there are too few active spots, and sufficient activity may not be obtained and it is not desirable.

[0020] Moreover, as for the surface amount of support mentioned above, it is desirable to consider as per [which are obtained / catalyst 1L for exhaust air gas cleanups / 120-300g]. the amount of support – per [1L] -- if the activity under high simian virus becomes inadequate in less than 120g and it exceeds 300g conversely, a bad influence, like bar diffusion of the reaction molecule to a lower layer and an interlayer, or pressure loss becomes large may arise, and it is not desirable

[0021] In addition, although you may be a non-processed thing, since it will stabilize more and the high catalyst of thermal resistance and endurance will be acquired if crystallinity is raised by performing hydrothermal processing and re-composition, it is desirable [the zeolite used for the interlayer and surface which were mentioned above remains as it is, and] to use the zeolite which performed such processing in this invention.

[0022] Moreover, what is necessary is just to multilayer by applying a zeolitic catalyst, a noble-metals component, etc. which were mentioned above to honeycomb-like support in this case, although the monolith support of a honeycomb configuration is used and multilayering of a lower layer, an interlayer, and a surface is realized with the catalyst of this invention. As this honeycomb material, although the thing of the quality of a cordierite is generally used widely, it is not limited to this and the honeycomb support which consists of a metallic material can also be used.

[0023] In addition, since the configuration of a catalyst can enlarge the touch area of the shape of a honeycomb then, a catalyst, and exhaust gas and pressure loss can also be suppressed, there is vibration, and it is advantageous especially when processing a lot of exhaust gas in the limited space uses as a catalyst for automobiles demanded.

[0024] Next, the manufacture method of the catalyst of this invention is explained. The honeycomb-like monolithic catalyst of this invention mixes catalyst powder with water, obtains a slurry, and can manufacture it by coating honeycomb support with this slurry. In this catalyst manufacture, as a raw material of the metal component supported to a zeolite, various compounds, such as the inorganic-acid salt of various metals, an oxide, organic acid chloride, a chloride, a carbonate, sodium salt, an ammonium salt, and an ammine complex compound, can be used, and it can support with methods usually used, such as an ion-exchange method and the sinking-in method.

[0025] In addition, although a desirable result can be obtained by using a metal raw material in many cases with a solution, adding an acid or a base in the solution, and adjusting pH suitably when based on the usual ion-exchange method and the sinking-in method, this invention is not restricted by such supporting method.

[0026] Although the catalyst for exhaust air gas cleanups of this invention explained above shows a cleaning effect to the exhaust gas from the internal combustion engine with which an air-fuel ratio is operated on 14.7 or more RIN conditions, especially an oxygen density is 5% or more, and if a HC/NOx ratio circulates and contacts ten or less exhaust gas for this catalyst, an efficient exhaust air gas cleanup will be realized. Moreover, although this catalyst is fully equal also to prolonged use under such exhaust gas conditions and a high purification performance is maintained, when an oxygen density is low and there are too many amounts of HC, coking to a catalyst front-face top becomes easy

to happen, and degradation of a catalyst may be promoted.

[0027]

[Example] Hereafter, although an example and the example of comparison explain this invention still in detail, this invention is not limited to these examples.

[0028] (Example 1)

(1) the inside of the airstream after adding the powder of an activated alumina, agitating and drying at 120 degrees C in a lower layer formation dinitrodiammine platinum solution for 8 hours -- 500 degrees C -- 2 hours -- calcinating -- platinum -- about 1.0 wt(s)% -- supported Pt-activated-alumina powder was obtained This powder, a nitric-acid acid alumina sol, and water were put into the magnetic ball mill pot, it mixed and ground for about 20 minutes, and the slurry of Pt-activated alumina was obtained. In addition, the addition of the alumina sol in this case was made into 5wt (s)%.

[0029] Thus, after applying the obtained slurry to nature honeycomb support of cordierite 1.0L with about 400 passage per 1 square inch cross section and carrying out hot air drying at 150 degrees C, it calcinated at 500 degrees C for 1 hour, and the honeycomb catalyst of coat **** 35 g/L was obtained. After dipping this honeycomb catalyst in the mixed-water solution containing a calcium acetate, a barium acetate, and a lanthanum nitrate and drying at 120 degrees C, it calcinated at 500 degrees C for 1 hour, and the honeycomb catalyst A1 which supported per [of 0.1 mols of each 1L of honeycomb catalysts, 0.15 mols, and 0.1 mols for calcium, barium, and the lanthanum was obtained.

[0030] (2) An alumina sol and water were added to the powder of the H type beta zeolite of about 35, and an interlayer's formation silica / alumina ratio put into the magnetic ball mill pot, mixed and ground for about 20 minutes, and obtained the slurry of beta zeolite. In addition, the addition of the alumina sol in this case was made into 8wt(s)% as aluminum 2O3. Subsequently, after applying the obtained slurry to the above-mentioned honeycomb catalyst A1 and carrying out hot air drying at 150 degrees C, it calcinated at 500 degrees C for 1 hour, and the honeycomb catalyst A2 which carried out the laminating of the interlayer of about 55 g/L on the lower layer of a honeycomb catalyst A1 was obtained.

[0031] (3) After the silica / alumina ratio could add the powder of about 35 NH4 type MFI zeolite and agitated in the copper nitrate of completion concentration 0.17M of surface formation and a three-layer laminating catalyst, and the cobalt-nitrate mixed-water solution (copper : cobalt = 8:2), it filtered and separated solid-liquid. This churning / filtration operation was repeated 3 times, and the MFI zeolite-catalyst cake which carried out ion-exchange support of copper and the cobalt was obtained.

[0032] The obtained cake was dried at 120 degrees C for 24 hours or more, subsequently it calcinated at 600 degrees C under air atmosphere for 4 hours, and the Cu-Co-MFI catalyst powder with which had copper 3.9wt(s)% and cobalt had 0.8wt(s)% supported was obtained. This catalyst powder was mixed with an alumina sol and water, the magnetic ball mill pot ground for 20 minutes, and it considered as the slurry. Thus, after coating the above-mentioned honeycomb-like catalyst A2 with the obtained slurry and drying at 120 degrees C for 8 hours, it calcinated at 450 degrees C among the airstream for 1 hour, and the three-tiered structure catalyst of the example 1 which carried out the laminating of the surface of about 200 g/L on the interlayer of a catalyst A2 was acquired.

[0033] (Example 2) Except that the silica / alumina ratio replaced surface MFI zeolite powder with about 42 NH4 type beta zeolite, the same operation as an example 1 was repeated, and the catalyst of this example was acquired.

[0034] (Example 3) Except having replaced with Pt support 1.0wt% which is the amount of noble-metals support in a lower layer to Pd support 1.2wt% and Rh support 0.2wt%, the same operation as an example 1 was repeated, and the catalyst of this example was acquired.

[0035] (Example 4) Except having replaced with 0.01 mols of magnesium, 0.01 mols of barium, and 0.01 mols of potassiums 0.1 mols of calcium, 0.15 mols of barium, and 0.1 mols of lanthanums which are contents, such as alkali metal in a lower layer, the same operation as an example 1 was repeated, and the catalyst of this example was acquired.

[0036] (Example 5) Except having replaced with 0.2 mols of barium, 0.05 mols of strontium, 0.04 mols of caesium, and 0.29 mols of ceriums 0.1 mols of calcium, 0.15 mols of barium, and 0.1 mols of lanthanums which are contents, such as alkali metal in a lower layer, the same operation as an example 1 was repeated, and the catalyst of this example was acquired.

[0037] (Example 6) Except having replaced amount of surface coats 200 g/L with 130 g/L, the same operation as an example 1 was repeated, and the catalyst of this example was acquired.

[0038] (Example 7) Except having replaced amount of surface coats 200 g/L with 280 g/L, the same operation as an example 1 was repeated, and the catalyst of this example was acquired.

[0039] (Example 8) Except having replaced amount of interlayer coats 55 g/L with 25 g/L, the same operation as an

example 1 was repeated, and the catalyst of this example was acquired.

[0040] (Example 9) Except having replaced amount of interlayer coats 55 g/L with 96 g/L, the same operation as an example 1 was repeated, and the catalyst of this example was acquired.

[0041] (Example 10) Except that the silica / alumina ratio replaced the surface MFI zeolite with the H type MFI zeolite of about 24, the same operation as an example 1 was repeated, and the catalyst of this example was acquired.

[0042] (Example 11) Except that the silica / alumina ratio replaced the surface MFI zeolite with the H type MFI zeolite of about 76, the same operation as an example 1 was repeated, and the catalyst of this example was acquired.

[0043] (Example 1 of comparison) Except having carried out the laminating of the surface on the lower layer, without preparing an interlayer, the same operation as an example 1 was repeated, and the catalyst of this example was acquired.

[0044] (Example 2 of comparison) Except having replaced an interlayer's beta zeolite with the gamma alumina, the same operation as an example 1 was repeated, and the catalyst of this example was acquired.

[0045] (Example 12) Except having replaced 0.01 mols of magnesium in a lower layer, 0.1 mols of barium, and 0.01 mols of potassiums with 0.03 mols of magnesium, 0.04 mols of barium, and 0.01 mols of potassiums, the same operation as an example 4 was repeated, and the catalyst of this example was acquired.

[0046] (Example 13) Except having replaced 0.2 mols of barium in a lower layer, 0.05 mols of strontium, 0.04 mols of caesium, and 0.29 mols of ceriums with 0.3 mols of barium, 0.02 mols of strontium, 0.3 mols of caesium, and 0.01 mols of ceriums, the same operation as an example 5 was repeated, and the catalyst of this example was acquired.

[0047] (Example 14) Except having replaced amount of surface coats 130 g/L with 100 g/L, the same operation as an example 6 was repeated, and the catalyst of this example was acquired.

[0048] (Example 15) Except having replaced amount of surface coats 130 g/L with 320 g/L, the same operation as an example 6 was repeated, and the catalyst of this example was acquired.

[0049] (Example 16) Except having replaced amount of interlayer coats 25 g/L with 17 g/L, the same operation as an example 8 was repeated, and the catalyst of this example was acquired.

[0050] (Example 17) Except having replaced amount of interlayer coats 25 g/L with 115 g/L, the same operation as an example 8 was repeated, and the catalyst of this example was acquired.

[0051] (Example 18) Except that the silica / alumina ratio replaced the surface MFI zeolite with the H type MFI zeolite of about 17, the same operation as an example 10 was repeated, and the catalyst of this example was acquired.

[0052] (Example 19) Except that the silica / alumina ratio replaced the surface MFI zeolite with the H type MFI zeolite of about 82, the same operation as an example 10 was repeated, and the catalyst of this example was acquired.

[0053] (Example 1 of a catalyst performance test) It included in the exhaust air system of engine DYNAMO equipment which installed the 4-cylinder 2.5L diesel power plant which is an example of a lean burn engine about the catalyst of each above-mentioned example, and rapid durable processing of 30 hours was performed at 630 degrees C.

Subsequently, it included in the exhaust air system of the same NJIN DYNAMO equipment as the above of the catalysts of each example processed in this way, and the NOx inversion performance at the time of a temperature up with a catalyst inlet temperature of 100 degrees C - 500 degrees C was measured. Under the present circumstances, the 100-500-degree C programming rate was [2.8 and the gas space velocity of the average HC/NOx ratio in about 30 degrees C / min, and exhaust gas] 45000h-1. In addition, with this engine DYNAMO equipment, gas oil can be poured in from the nozzle prepared between the engine manifold and the catalyst, and it is possible to change HC/NOx in exhaust gas by this. The average NOx purification performance in 100-500-degree-C temperature up about the catalyst of each example is shown in Table 1.

[0054]

[Table 1]

触媒	平均NOx浄化率(%)
実施例1	26.4
実施例2	27.5
実施例3	25.5
実施例4	21.6
実施例5	19.4
実施例6	18.9
実施例7	26.1
実施例8	21.4
実施例9	18.8
実施例10	17.7
実施例11	24.4
実施例12	17.0
実施例13	17.3
実施例14	16.9
実施例15	17.5
実施例16	17.3
実施例17	18.5
実施例18	16.4
実施例19	18.1
比較例1	12.4
比較例2	13.3

[0055] Although the catalyst of the example belonging to the range of this invention is compared with the catalyst of the example of comparison from Table 1 and the rate of NOx purification is high, the catalyst of an example carries out the trap of the HC efficiently in a low-temperature region, and this is considered that it being efficient and using these HC in temperature up process is shown. moreover, if the amounts of support, such as alkali metal, deviate from the suitable range, the effect of a lower layer or a surface will decrease – there are things, especially the silica / alumina ratio of a surface zeolite are understood that the influence which it has on a catalyst performance is also large. Furthermore, it is in Ming to be [of an interlayer and a surface] also the amount of coats and that the influence which it has on a catalyst performance is also large.

[0056] (Example 2 of a catalyst performance test) The same purification performance test as the example 1 of an examination mentioned above was performed using the catalyst of an example 2. However, in this performance test, by changing HC concentration in exhaust gas, the HC/NOx ratio was changed in 2-15, light-off-Right On was repeated 10 times, and it asked for the rate of NOx average purification to a subsequent HC/NOx ratio. The obtained result is shown in drawing 1.

[0057] With the catalyst for exhaust air gas cleanups of this invention, drawing 1 showed that the rate of NOx purification fell rapidly, when the HC/NOx ratio became [the HC/NOx ratio] larger than 10, while the rate of

purification high enough was obtained or less in ten. This result shows that the catalyst of this invention realizes the high rate of NOx purification in the moderate amount of HC rather.

[0058] (Example 3 of a catalyst performance test) The same purification performance test as the above-mentioned example 1 of an examination was performed using the catalyst of an example 2. However, in this performance test, it carried out by having changed the oxygen density of exhaust gas in 2% - 10% of range, and having repeated light-off-Right On 10 times, the light-off-Right On test was performed after that, and it asked for the rate of average purification of NOx. The obtained result is shown in drawing 2.

[0059] Although the catalyst for exhaust air gas cleanups of this invention demonstrated the high rate of NOx purification when the oxygen density of exhaust gas repeated the light-off-Right On test under 5% or more of conditions with comparatively many amounts of oxygen, drawing 2 showed that sufficient NOx purification performance might not be shown, when the light-off-Right On test was repeated under conditions with few oxygen densities than 5%.

[0060]

[Effect of the Invention] As explained above, according to this invention, the catalyst for exhaust air gas cleanups and the purification method of having written arranging three catalyst beds which have a specific function on honeycomb support, and having raised sharply the NOx decontamination capacity in the RIN exhaust gas in a low-temperature region and a low HC/NOx ratio, and having prevented degradation of a catalyst under the high-temperature-hot-water heat condition can be offered.

[0061] That is, if the catalyst for exhaust air gas cleanups of this invention is used, it will also become possible to realize the automobile was a low-temperature region 150 degrees C or less, and environmental pollution excelled [automobile] also in economical efficiency few suitable for a lean burn engine as for this catalyst since it was efficient and RIN exhaust gas was purified also in a low HC/NOx ratio.

[Translation done.]

* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The catalyst for exhaust air gas cleanups which is characterized by providing the following and which carries out the laminating of a lower layer, an interlayer, and the surface one by one, and changes on honeycomb-like monolith support. At least one sort of components chosen from the group to which the above-mentioned lower layer changes from platinum, palladium, and a rhodium. At least one sort of components chosen from the group which consists of alkali metal, alkaline earth metal, and rare earth elements are contained, the above-mentioned interlayer contains beta zeolite, and the above-mentioned surface is copper and/or cobalt.

[Claim 2] The catalyst for exhaust air gas cleanups according to claim 1 characterized by the above-mentioned alkali metal, alkaline earth metal, and rare earth elements being at least one sort of things chosen from the group which consists of magnesium, calcium, a potassium, barium, a lanthanum, strontium, caesium, and a cerium.

[Claim 3] The catalyst for exhaust air gas cleanups according to claim 1 or 2 to which the content of at least one sort of components chosen from the group which consists of the above-mentioned alkali metal, alkaline earth metal, and rare earth elements is characterized by being the 0.1-0.6 mols of the catalyst 1L scaling for exhaust air gas cleanups concerned.

[Claim 4] The catalyst for exhaust air gas cleanups given in any one term of the claims 1-3 characterized by the silica / alumina ratio of the above-mentioned beta zeolite being 20-150.

[Claim 5] The catalyst for exhaust air gas cleanups given in any one term of the claims 1-4 characterized by the above-mentioned interlayer's amounts of support being per [the catalyst 1L for exhaust air gas cleanups concerned / 20-100g].

[Claim 6] The catalyst for exhaust air gas cleanups given in any one term of the claims 1-5 characterized by the silica / alumina ratio of the zeolite which the above-mentioned surface contains being 20-80.

[Claim 7] The catalyst for exhaust air gas cleanups given in any one term of the claims 1-6 characterized by the amounts of support of the above-mentioned surface being per [the catalyst 1L for exhaust air gas cleanups concerned / 120-300g].

[Claim 8] It is the exhaust air gas cleanup method using the catalyst for exhaust air gas cleanups given in any one term of the claims 1-7. The above-mentioned catalyst for exhaust air gas cleanups is installed in the exhaust air system of the internal combustion engine with which an air-fuel ratio is operated or more by 14.7. an oxygen density for this catalyst for exhaust air gas cleanups at 5% or more And the exhaust air gas cleanup method characterized by for the HC/NO_x ratio which is the ratio of the amount of hydrocarbons required for nitrogen oxide and a hydrocarbon to react and convert nitrogen oxide into nitrogen and the amount of nitrogen oxide circulating, and contacting ten or less exhaust gas.

[Translation done.]